Structure and dynamics of water at the Pt(111) interface: Molecular dynamics study

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We prescribe an analytical form of the interaction potential between rigid water and a rigid platinum metal surface, which takes into account the surface symmetry and corrugation. Using this potential we perform a molecular dynamics computer simulation on water lamina restricted by two Pt(111) surfaces and investigate the structure and dynamics of water at the Pt interface. At 300 K the water layer adjacent to the metal surface displays solid-like properties. Patches of ice-like structure embedded in this layer are observed in the simulation. The next two layers of water display ordering similar to ice-I. Beyond these three layers the structure and dynamics of water are bulk-like.

I. INTRODUCTION

A detailed molecular level description of structure and dynamics of water next to metallic surfaces is of a fundamental importance for electrochemistry, catalysis, and corrosion studies. Structural details about water monolayer-metal surface interface can be obtained using different experimental techniques, described in a review by Thiel and Madey.¹ In the case of bulk water-metal interfaces, where no molecular level information is available from experiment, computer simulations can play a very significant role. To perform a simulation on water-metal interfaces one has to know water-water and water-metal interaction potentials. While the form of the water-water potential can be chosen from a variety of the potentials described in the literature,² the form of the water-metal interaction potential is not well established. Of particular interest to us is the interaction potential between water and catalytically and electrochemically important metal such as Pt. Very often to represent the water-metal interaction an image charge method based on continuum electrostatics is used in the simulations.^{3,4} The recent simulations clearly demonstrate the failure of this method to predict correctly the orientational properties of water molecules adsorbed on the surface of the transition metal. Thus the computer simulations predict that the adsorbed water molecule orients one of its hydrogens towards the surface,⁴ while the experimental observations indicate that water tends to situate with its oxygen atom located next to the metallic surface and its hydrogens pointing away.¹ Theoretical calculations on bonding of water to transition metal clusters support the experimental conclusions.^{5,6} The calculations also reveal that chemisorption of water to the surface of the transition metal is due to the overlap of the metal *d* orbitals with the lone pair of water. That explains the orientation of water on the transition metal surface.⁵ Based on one of such calculations of water on Pt cluster,⁶ Spohr and Heinzinger developed an interaction potential for water-platinum atom.⁷ Although obtained from a cluster calculation, the Spohr and Heinzinger potential correctly predicts the adsorption of water on the top site of the Pt metal surface and exhibits a minimum for orientations with the oxygen atom

closer to the surface than the hydrogen atoms. It also predicts the correct order of magnitude of the adsorption energy and the adsorption distance. Using this potential, Spohr performed a molecular dynamics simulation of a slab of water between two Pt (100) surfaces.⁸ In Spohr's simulation the Pt surfaces were explicitly represented by 550 Pt atoms and the dynamics of these atoms was included in the calculation. Recently we have developed a water-platinum surface potential,⁹ which takes into account the symmetry of Pt surface and its corrugation. This potential allowed us to concentrate on the motion of water molecules only, replacing all Pt atoms by an effective external field. In addition we have used a rigid water model in our simulation while Spohr used a flexible model. Comparison of structural data from our simulation with Spohr's simulation of water at Pt (100) interface displayed a very good agreement between these two simulations. The advantage of our approach is that it results in the substantial saving of the computational time and therefore permits us to perform simulations on larger size systems and over longer time periods. For example, due to the symmetry in the problem, the water/Pt(111) interface simulation described below demands a consideration of a large number of water molecules in the molecular dynamics unit cell (see Sec. III), therefore our method turned out to be very helpful in the present simulation. We also anticipate that our approach will play an important role in the future studies of the aqueous ionic solutions at the interfaces, where long simulations are necessary.

In Spohr's work and in our initial work only water/Pt (100) interface was considered, while many of the experimental data are available for water/Pt (111) interface.¹ This interface is also more interesting, since the Pt-Pt nearest-neighbor distance is commensurate with the water-water distance and Pt(111) surface is hexagonal; all these facts favor creation of ice structure at the interface. Such ice-like structure was observed in high-vacuum studies of water layers on Pt surface at temperatures around 150 K.¹ The main motivation for our present study was to see how much of this ice structure remains at the interface of bulk water and Pt (111) surface at room temperature.

TABLE I. The parameters for H₂O–Pt(111) potential.

kJ/mol	nm ⁻¹
$A_1 = 16.094$	$\beta_1 = 33.541$
$A_2 = -54.988$	$\beta_2 = 9.653$
$A_3 = -18.013$	$\beta_3 = 32.205$
$A_4 = 15.417$	$\beta_4 = 30.557$
$A_5 = -0.626$	$\beta_5 = 7.127$
$A_6 = -0.113$	$\beta_6 = 14.357$
$A_7 = 10.610$	$\beta_7 = 9.630$
$A_8 = 4.048 \times 10^{-2}$	$\beta_8 = 24.192$
$A_9 = 4.800 \times 10^{-4}$	$\beta_9 = 26.295$
$z_m = -1.233$ nm	

II. POTENTIAL ENERGY SURFACE

The multidimensional potential energy surface is represented by water–water and water–surface interaction potentials. The water–water potential we use in our simulation is determined by SPC/E model, which represents quite nicely bulk properties of water.^{10,11} The interaction of a water molecule with the surface is represented by the sum of the interactions of individual atoms in water and the surface, i.e.,

$$V_{\text{H}_2\text{O,Pt}} = V_{\text{H,Pt}} + V_{\text{H,Pt}} + V_{\text{O,Pt}} \quad (1)$$

The oxygen–Pt and hydrogen–Pt interactions are given by the following expressions:

$$V_{\text{O,Pt}} = f_0(z) + f_1(z)Q_1(x,y) + f_2(z)Q_2(x,y), \quad (2a)$$

$$V_{\text{H,Pt}} = g_0(z) + g_1(z)Q_1(x,y) + g_2(z)Q_2(x,y), \quad (2b)$$

where

$$Q_1(x,y) = \cos 2\pi s_1 + \cos 2\pi s_2 + \cos 2\pi s_3, \quad (3a)$$

$$Q_2(x,y) = \sin 2\pi s_1 + \sin 2\pi s_2 - \sin 2\pi s_3, \quad (3b)$$

and

$$s_1 = \sqrt{2}/a[x - y/\sqrt{3}], \quad (3c)$$

$$s_2 = 2\sqrt{2}y/(\sqrt{3} \cdot a), \quad (3d)$$

$$s_3 = s_2 + s_1. \quad (3e)$$

In Eqs. (3), $a = 0.392$ nm which is the Pt lattice constant. The functional forms of f and g are given by

$$f_0(z) = A_1 \exp[-\beta_1(z - z_m)] + A_2 \exp[-\beta_2(z - z_m)],$$

$$f_1(z) = A_3 \exp[-\beta_3(z - z_m)] + A_4 \exp[-\beta_4(z - z_m)],$$

$$f_2(z) = A_5 \exp[-\beta_5(z - z_m)] + A_6 \exp[-\beta_6(z - z_m)],$$

$$g_0(z) = A_7 \exp[-\beta_7(z - z_m)],$$

$$g_1(z) = A_8 \exp[-\beta_8(z - z_m)],$$

$$g_2(z) = A_9 \exp[-\beta_9(z - z_m)]. \quad (4)$$

In the above Eqs. (4) the values of the parameters were obtained by a fit to the Spohr–Heinzinger potential⁷ and are given in Table I. In Eqs. (3) and (4) x, y, z are coordinates of the atom in the water molecule.

FIG. 1. A portion of fcc Pt(111) surface illustrating different binding sites. Solid circle represents the a-top site (site A); the crosshatched circle represents the threefold hollow site (site B) under which there is a Pt atom in the second layer. The circle with a plus sign represents the threefold hollow site (site C) under which there is no Pt atom in the second layer. The midpoint of the solid line connecting two a-top sites represents the bridge site (site D).

On a Pt(111) surface one can distinguish four binding positions for the water molecule (see Fig. 1). The preferential adsorption site is on the top of platinum atom (site A) with an adsorption energy of -40.7 kJ/mol. The energies of adsorption on hollow sites B and C are -27.1 and -23.9 kJ/mol, respectively, while the adsorption energy on bridge site D is -26.1 kJ/mol. These energies are in qualitative agreement with the recently calculated energies of adsorption of H₂O on Ni(111).¹² To provide a general picture of the water–Pt(111) interaction its potential is displayed in Figs. 2 and 3. Figure 2 displays the variation

FIG. 2. Interaction potential for water–Pt(111) surface shown for different binding sites as a function of distance along the normal to the Pt surface. (a) a-top site; (b) hollow site B; (c) hollow site C; (d) bridge site.

FIG. 3. (a) Potential energy contours for the water-Pt(111) interaction. (x axis: -0.59 to 0.59 nm; y axis: -0.4 to 0.4 nm). The contours are obtained using Eqs. (1)–(4) with parameters given in Table I. The values of the potential at points represented by a, b, and c are -40 , -27.1 , and -23.9 kJ/mol, respectively. (b) Same as Fig. 3(a) only obtained from the potential given in Ref. 7.

of the water-Pt(111) potential in the z direction (the direction perpendicular to the plane of Pt surface), while the contour plot of the shape of the interaction potential in the x,y plane can be seen in Fig. 3(a). Figure 3(b) shows the contour plot obtained by using the Spohr-Heinzinger potential which involves explicit summation of contributions from every H_2O -Pt atom interaction. Interaction of one water molecule with 2688 atoms of Pt arranged in fcc(111) structure was included in the sum. Comparison of Figs. 3(a) and 3(b) shows that our fit reproduces rather well the symmetry and shape of the H_2O -Pt(111) surface interaction.

III. MOLECULAR DYNAMICS SIMULATION

To study structural and dynamical properties of the water-Pt interface a molecular dynamics simulation of SPC/E water bounded by two Pt (111) surfaces was performed. Since the interatomic distance between Pt atoms (~ 0.277 nm) is commensurate with the distance between water molecules in ice and the hexagonal structure of the lattice is capable of promoting ice structure we had to find a unit cell which will not obstruct a possible creation of ice-like structures at the interface. Therefore, we have chosen a hexagonal prism as our molecular dynamics box with

FIG. 4. Ideal structure of water bilayer on the surface of fcc Pt(111). The crosshatched oxygens belong to the first layer of the bilayer and are flip-up. The water molecules that have “+” sign belong to the second layer and are flop-down. The rest of the water molecules in the second layer are flip-up with one of the hydrogens pointing in z direction away from the Pt surface.

the hexagon as its base. The hexagonal base serves as a unit cell for a two-dimensional ice-like structure of water on the Pt(111) surface and it is shown in Fig. 4. This structure, which allows the maximum coverage of the surface, was proposed by Doering and Madey.¹³ As one can see from Fig. 4, the idealized structure of water on the Pt(111) surface is actually a bilayer with the first layer of the bilayer having all molecules in a “flip-up” position (a position in which water molecules have their dipoles pointing away from the surface), while the second layer hydrogen bonded to the first layer is made up of flip-up and flop-down water molecules (with dipole moments pointing towards the surface).

The dimensions of the molecular dynamics box are as follows: The length of the hexagon side in the base is 2.24 nm. In order to satisfy the form of water-Pt interaction potential given by Eqs. (1)–(4) with parameter values from Table I we had to place the first layer of Pt atoms at distances $|z| = 1.5$ nm from the center: therefore we may say that the distance between Pt surfaces is 3 nm. The total number of water molecules in the simulation was adjusted until the density in the middle of the box was equal to the bulk density (1 g/cm^3). That resulted in a total number of 1298 water molecules in our simulation. The simulation was run for 20 ps of equilibration time followed by 40 ps of production run. The time step used was 2.5 fs. The molecular dynamics Verlet algorithm¹⁴ with the Shake routine¹⁵ was used to propagate the trajectories. A minimum image convention was used to calculate the interactions. Periodic boundary conditions, modified to account for the hexagonal shape of the unit cell, were used in x and y directions. Since the size of the cell was rather large the long-range forces contribution was not included in the simulation. The temperature of the simulation was 300 K.

FIG. 5. Oxygen (solid line) and hydrogen (dotted line) density profiles obtained from our simulation.

IV. RESULTS

A. Structure

The oxygen and hydrogen density profiles obtained from the simulation are displayed in Fig. 5. The plot demonstrates that the results obtained from the right and the left part of the simulation box are symmetric as should be expected. The oxygen density profile clearly shows two well separated peaks next to the Pt surface. The first peak corresponds to an adsorbed water layer and the second peak is due to a layer that is hydrogen bonded to it. Although not as prominent as the two peaks next to the surface, a third peak corresponding to the third layer can also be distinguished. The first water layer, L1, located at $1.10 \text{ nm} < |z| < 1.35 \text{ nm}$ has an average density of 1.47 g/cc and the average number of water molecules in this layer is 158, which is close to the 150 water molecules in the ideal structure (see Fig. 4). The second layer, L2, occupies the region $0.84 \text{ nm} < |z| < 1.10 \text{ nm}$; its average density is 1.09 g/cc . The third layer, L3, occupies the region $0.46 < |z| < 0.84 \text{ nm}$ and has the bulk density.

The density profiles from Fig. 5 and the orientational distributions from Fig. 6 are instrumental in reconstruction of water structure in the lamina. To find more details on this structure, the layer L1 was divided into two sublayers and the orientational distribution of angles between the water dipole vector and the normal vector pointing into the Pt surface along the z direction was calculated. Also a distribution of angles between the OH vector and surface normal vector was calculated. These two distributions are reproduced in Fig. 6 together with the distribution for other sublayers. For the first sublayer of the first layer ($1.25 \text{ nm} < |z| < 1.35 \text{ nm}$) most of the molecules have their dipole moments pointing slightly away from the surface and OH vectors are mostly parallel to the surface with a slight tilt. That means that most of the molecules of the first sublayer are flip-up type molecules. The distribution of

FIG. 6. Distributions of dipole (solid line) and OH (dotted line) orientations as a function of $\cos \Theta$ (Θ is the angle between the dipole or OH vector and the inward normal to the metal surface). (a) $1.25 < z < 1.35 \text{ nm}$; (b) $1.15 < z < 1.25 \text{ nm}$; (c) $1.05 < z < 1.15 \text{ nm}$; (d) $0.95 < z < 1.05 \text{ nm}$; (e) $0.85 < z < 0.95 \text{ nm}$; (f) $0.72 < z < 0.85 \text{ nm}$; (g) $0.59 < z < 0.72 \text{ nm}$; (h) $0.46 < z < 0.59 \text{ nm}$; (i) $0.0 < z < 0.14 \text{ nm}$;

dipole moments for the second sublayer ($1.15 \text{ nm} < |z| < 1.25 \text{ nm}$) is bimodal which clearly indicates that the sublayer has flip-up and flop-down molecules. Flop-down molecules are hydrogen bonded to flip-up molecules of the first sublayer and the hydrogen atoms of flip-up molecules of the second sublayer of the first layer are hydrogen bonded to the second layer. These are the hydrogens which give a small peak in the hydrogen density profile curve in the region $1.12 \text{ nm} < |z| < 1.18 \text{ nm}$. The second small hydrogen peak in the region $1.02 \text{ nm} < |z| < 1.12 \text{ nm}$ is due to the hydrogens of the second layer. The positions of the peaks for the dipole orientation curves indicate that the planes of water molecules in the first layer are close to being parallel to the surface. Therefore if the hexagonal ice-like structure of water next to the surface exists, it should be mostly flat, with a very slight puckering.

To study the structure of the wider second layer we have divided it into three sublayers. The first sublayer of the second layer ($1.05 \text{ nm} < |z| < 1.15 \text{ nm}$) includes all those water molecules which serve as a bridge between layers L1 and L2 and there are not many of them. Most of the water molecules are found in the second and third sublayers of the second layer. The OH vector distribution and dipole distribution of the second sublayer of the second layer display an enhanced probability for the water molecule to point one of the OH vectors directly into the wall. Simultaneously, the second OH vector is pointing away from the wall in the direction that makes a tetrahedral angle towards the first OH bond. The orientational distributions of the second and third sublayers of L2 are mirror images of one another with respect to $\cos \Theta = 0$. Such behavior is expected if water would have an ice-I structure with the c axis along the z direction. Although the orientational distributions for these two sublayers in our simulations are broad, the maxima correspond to what would

be expected for distributions in ice-I structure. In addition, we have also noticed that the distance between the second and third layers in our simulation is 0.35 nm, which is the distance between layers in ice-I structure, and that the third layer has orientational distributions reminiscent of the second layer. Based on the preceding discussion we propose that water in the second and third layers displays an ordering similar to that of ice-I. Similar ordering was observed by Lee *et al.*¹⁶ in their simulation of water next to a hydrophobic wall.

To summarize, the following structure of water next to Pt(111) surface is proposed. At the surface around 80% of available adsorption sites are occupied by water. This value is consistent with the number from the ideal structure proposed by Doering and Madey.¹³ In the ideal structure one observes regularly distributed patches of ice which are densely packed together. We have also observed some patching of hexagonal ice-like structures in our simulation (see below). Moving in the *z* direction into bulk the orientational and lateral ordering of water is not completely homogeneous and is biased towards the ordering observed in ice-I structure with its *c* axis directed along *z* direction. We believe that water has bulk-like structure beyond the third layer, although the dipole orientation plot shows slight anisotropy even in the middle of the lamina. This is similar to the nonuniformity of orientational properties observed by Valleau and Gardner.¹⁷ We think that this preference is related to the use of minimum image boundary conditions in the simulations, although the possibility that the box length is not large enough should not be excluded.

One of the interesting questions related to the structure of hexagons of water on the surface is the following: Given a hexagon what is its predominant conformation while adsorbed on the Pt(111) surface? For the hexagon ring one can distinguish between so-called "boat" and "chair" configurations. The following is an explanation of a means by which the hexagonal rings can be separated into families of "boat-like" and "chair-like" configurations.

The six dihedral angles of the hexagonal ring were focused on as variables determining the ring's conformation. Boats are readily distinguished from chairs by comparing their respective dihedral angle patterns. In the typical chair, the dihedral angles alternate between positive and negative values of equal magnitude as one goes around the ring, e.g., (-30° , $+30^\circ$, -30° , $+30^\circ$, -30° , $+30^\circ$). In the perfect boat conformation, a cyclical pattern of three angle values exists consisting of one positive and one negative value of equal magnitude and a third angle of 0° , i.e., (30° , -30° , 0° , 30° , -30° , 0°) or (0° , -30° , 30° , 0° , -30° , 30°) and all cyclic permutations. A "flat" or "coplanar" ring is neither a boat nor a chair; all of a flat ring's dihedral angle values are identically zero.

An arbitrary hexagonal ring in thermal motion is seldom configured to match the descriptions of a perfect chair, boat, or flat ring. Consequently, *ad hoc* rules had to be drawn up to enable the characterization of rings into three categories. The rules employed were: (1) a hexagon having at least three dihedral angle values with absolute values less than 10° was considered flat, (2) a hexagon

TABLE II. Conformational analysis of hexagons in the ice-like patches.

Cutoff angle (deg)	hexagon #	# of "boats"	# of "chairs"	# of "flats"
10	1	3	2	35
	2	4	0	36
	3	0	1	39
20	1	0	1	39
	2	4	0	36
	3	0	1	39

having three positive and three negative dihedral angle values alternately interspersed and with no dihedral angle absolute values less than 10° was considered a chair, (3) a hexagon with two dihedral angle values less than -10° , two dihedral angle values greater than $+10^\circ$, and two with absolute values less than 10° , cyclically disposed was considered a boat, (4) a hexagon not fitting any of the three descriptions above was considered flat.

We have performed a conformation analysis on the three hexagon rings, which are members of an ice-like patch on the surface. The analysis was done using 40 conformations, each separated by 0.25 ps, and the results are presented in Table II. Since the cut-off angle discussed above (10° angle) is arbitrary, we present the results for two values of this angle: 10° and 20° . While the quantitative results do depend on the value of the angle, the qualitative result is independent of it. Most of the hexagons are flat, as we have anticipated it. This is due to the strong water-Pt interaction, which flattens the hexagon ring. When the ring is not flat it prefers a boat conformation.

B. Dynamics

Perhaps the most illustrative expositions of the structure and dynamics of water in our simulation are the scatter plots in Figs. 7(a)–7(d). In these figures a dot has been drawn every 0.25 ps at the (*x*,*y*) position of each oxygen atom. Figure 7(a) depicts positions of waters in the *xy* plane for the L1 layer, 7(b) for L2 layer, 7(c) for L3 layer, and 7(d) for the 0.35 nm layer in the middle of the box. The molecules in layer L1 repeat the structure of the underlying fcc Pt(111) surface and their motions are mostly oscillations about equilibrium positions. While for the second layer some ordering is still observed and the configuration space coverage is not homogeneous, the density distribution looks more like that in L3. To have some quantitative estimates related to the diffusional motion of water molecules, we have calculated apparent diffusion coefficients for molecules in L1, L2, L3 and in the middle of

TABLE III. Effective diffusion coefficients for different bins. (in units of 10^{-5} cm²/s).

	L1	L2	L3	LB
D_{xy}	<0.1	1.58	2.20	2.46
D_z	<0.1	0.14	1.06	1.95

FIG. 7. Projection of positions of oxygen atoms on the xy plane (plane parallel to the Pt surface) for four different layers of water at different distances from the metal surface. (a) adsorbate layer ($1.10 < z < 1.35$ nm); (b) second layer ($0.84 \text{ nm} < z < 1.10$ nm); (c) third layer ($0.46 \text{ nm} < z < 0.84$ nm); (d) fourth layer ($0.0 \text{ nm} < z < 0.35$ nm). The particle trajectories are 10 ps long.

the box. The mean square displacements in x and in z directions for each of these four layers are represented in Fig. 8, and the effective diffusion coefficients obtained from the formulas

$$D_{xy} = \lim_{t \rightarrow \infty} \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{4t},$$

$$D_z = \lim_{t \rightarrow \infty} \frac{\langle \Delta z^2 \rangle}{2t}$$

are given in Table III.

FIG. 8. Mean square displacement in x and z directions as a function of time for different bins in the simulation box. $\square$: $\langle x^2(t) \rangle$ in a bin where $|z| < 0.46$ nm; $\circ$: $\langle z^2(t) \rangle$ for $|z| < 0.46$ nm; $\triangle$: $\langle x^2(t) \rangle$ for $0.46 \text{ nm} < z < 0.84$ nm; ∇ : $\langle z^2(t) \rangle$ for $0.46 \text{ nm} < z < 0.84$ nm; $\diamond$: $\langle x^2(t) \rangle$ for $0.84 \text{ nm} < z < 1.10$ nm; $\blacksquare$: $\langle z^2(t) \rangle$ for $0.84 \text{ nm} < z < 1.10$ nm; $\bullet$: $\langle x^2(t) \rangle$ for $1.10 \text{ nm} < z < 1.35$ nm; $\blacktriangle$: $\langle z^2(t) \rangle$ for $1.10 \text{ nm} < z < 1.35$ nm.

FIG. 9. Same as Fig. 7(a). The hexagonal ice-like patches are shown explicitly.

In our calculations of mean square displacement in the layer, we considered the molecule as belonging to the layer even when the molecule crossed the boundaries of the layer, as long as it remained outside no longer than 1 ps. No substantial diffusion is observed in the layer next to the wall, while a large anisotropy in the diffusion coefficient is observed for the second layer. As one can see the water molecules in L2 are more mobile in the direction parallel to the metal surface than in the perpendicular direction. The anisotropy in diffusion is greatly reduced for the third layer and nearly disappears for molecules in the bulk-like part of the box. Some degree of anisotropy still remains in the bulk-like part of the box, which may be due to the way we calculate the effective diffusion coefficient, but it may also reflect the real dynamic anisotropy in the middle of the lamina.

A close look at the structure of water in Fig. 7(a) reveals the presence of hexagonal ice-like structures. Figure 9, which is just an enlarged Fig. 7(a), clearly displays patches of the hexagonal rings. These patches are similar to the ones present in the ideal structure from Fig. 4. To get a better feeling on the stability of ice-like patches next to the Pt surface we have looked at a few snapshots of the water structure in L1. We observed that the location of the ice-like patches was not changed but the number of hexagonal rings in the patch was changing with time.

Since there are empty adsorption sites on the Pt surface, there is a possibility for the motion of the water molecule from one adsorption site to the neighboring site. Indeed, we have observed such motion. To understand how such motion occurred we have followed a few trajectories of the particles that move from one adsorption site to another. In all cases we have considered, the molecules move away from the surface to the edge of layer L1, often recrossing into layer L2, where the rather fast (~ 1 ps) exchange of adsorption site occurs. A typical trajectory illustrating a water molecule hopping between two adsorption sites is shown in Fig. 10. In spite of this hopping motion between the neighboring sites, a patch of ice-like structure next to

FIG. 10. A typical trajectory showing the changes in x , y , and z coordinates for a water molecule hopping between two adsorption sites. Only oxygen atom coordinates are displayed.

the surface which was stable during the whole 40 ps of the simulation time was observed.

C. Hydrogen bonding

To get further insight into the structure and dynamics of water between Pt walls we have performed a layer-wise hydrogen bond analysis on the water coordinates generated by the simulation. We have considered three water layers: L1, L2 and LB—the layer next to the center ($0.0 \text{ nm} < |z| < 0.3 \text{ nm}$). The analysis was performed on 80 configurations from a 40 ps run. Two consecutive configurations were separated in time by 0.5 ps.

For each layer we have computed intermolecular energies for molecules that belong to the particular layer concerned and are within a distance of 0.323 nm. If the pair's interaction energy was below $V_{\text{H.B}} = -2.5 \text{ kcal/mol}$, we considered the pair to be hydrogen bonded. In Table IV we show the distribution of hydrogen bonds in different layers. It should be noted here that we have considered only those bonds for which both the molecules are in a single layer. That is why for layers L2 and L3 the peak is shifted to two hydrogen bonds per molecule, since other hydrogen bonds are made with the waters belonging to the neighboring layers. For the layer L1 the peak is on three hydrogen

TABLE IV. Distribution of hydrogen bonds per molecule.

n	Probability in:		
	L1	L2	LB
0	0.0022	0.0372	0.0638
1	0.0450	0.2432	0.3068
2	0.3248	0.4654	0.4309
3	0.4926	0.2395	0.1709
4	0.1307	0.0111	0.0080
5	0.0031	0.0000	0.0000

TABLE V. Distribution of hydrogen bonded polygons.

Size	Probability in:		
	L1	L2	LB
3	0.0799	0.0465	0.0941
4	0.1963	0.2095	0.2289
5	0.2056	0.3132	0.2510
6	0.2015	0.1646	0.1803
7	0.0852	0.0810	0.0982
8	0.0835	0.0707	0.0278
9	0.0597	0.0434	0.0378
10	0.0518	0.0378	0.0153
11	0.0366	0.0335	0.0041

bonds per molecule, which is in agreement with what one would get from the calculation performed on the idealized structure.

Using a recently developed scheme,¹⁸ we have enumerated nonshort circuited hydrogen bonded polygons (rings) for each layer. The distribution of these polygons is shown in Table V. We can clearly see the distinctly flat nature of the distribution in L1 as opposed to the distribution in L2 and LB, where the peak is on pentagonal species. Keeping in mind that we have considered only those polygons which are defined entirely within a single layer, we can understand the abundance of pentagons in L2 and LB since they are the most planar rings. Near the wall, in the L1 layer, due to the surface influence we find also four and six membered hydrogen bonded rings.

Although hydrogen bonded polygons are only transient structural species we thought it would be interesting to investigate if any of these species may be found stable enough to be detectable, especially near the wall. For this purpose we calculated polygon survival times by explicitly identifying unique rings in subsequent configurations. In Table VI we present the distribution of rings that survived for at least 0.5 ps. It also shows the maximum survival time defined by the longest time of survival of at least one member. As we can see in the layer nearest the wall at least one hexagon survived up to 12.5 ps whereas in layers L2 and L3 none survived more than 1.5 ps. It should also be pointed out that in the layer nearest the wall, although the hexagon survived for the longest duration, the survival

TABLE VI. Distribution of rings that survived at least 0.5 ps and maximum survival times.

Size	# of rings that survived at least 0.5 ps			Maximum survival times in ps		
	L1	L2	LB	L1	L2	LB
3	93	1	0	4.5	0.5	0.0
4	256	20	6	6.5	1.5	0.5
5	296	42	18	7.5	1.5	1.5
6	263	13	11	12.5	1.5	1.5
7	64	4	1	2.5	1.5	1.5
8	51	2	1	3.5	0.5	0.5
9	25	0	0	1.5	0.0	0.0

times for pentagons (7.5 ps), quadrangles (6.5 ps) or even triangles (4.5 ps) are also significant.

V. SUMMARY AND CONCLUSIONS

We have investigated the structure and dynamics of water confined between Pt(111) surfaces using a molecular dynamics computer simulations method, with particular emphasis on the behavior of water at the water/metal interface. We have derived an analytical form of the interaction potential for the H₂O/Pt(111) system which incorporates the corrugation of the Pt(111) surface. A hexagonal prism has been used as the simulation box instead of the cubic/rectangular box which is traditionally employed in molecular dynamics simulations. This was necessary in order to avoid the destruction of hydrogen bonding network along the *x,y* directions.

The oxygen and hydrogen density profiles along the direction perpendicular to the metal surface and orientational distributions for dipoles and OH vectors show that there are three ordered layers of water on the Pt(111) surface. The first layer which is adsorbed on the surface exhibits patterns in which water forms ice-like structures consisting of hexagons with the oxygens bound to Pt atoms on the surface. The second layer of water which is hydrogen bonded to the first layer of adsorbed water molecules also shows the static ordering influenced by the template effect of the Pt(111) surface through the adsorbed layer. Although not as prominent as the first two layers, there persists some ordering in the third layer of water that is hydrogen bonded to the second layer. Beyond this layer, transition to bulk behavior is noticed. The distributions of dipole and OH vectors, in conjunction with the density profiles, suggest that the displayed ordering is similar to the one observed in ice-I.

The analysis we carried out on the hydrogen bond network using an energetic criterion also supports the static ordering of the adsorbed layer. It was found that, in the adsorbed layer, six membered rings survive for a longer time than the fewer-membered rings, evidencing the influence of the template effect of the Pt(111) surface on the preferential creation of six membered rings among the water molecules. The ring structures formed in the second layer and beyond do not survive as long as the ones in the adsorbate layer.

The results from our present and our previous simulation⁹ and the results from the simulations of water at the interface with its vapor,¹⁹ or at the interface with the hydrophobic surface¹⁶ clearly show that the detailed knowledge of the interaction potential between water molecules and the molecules on the other side of interface is of pivotal importance. If this is the case, then how reliable is the potential we use in our simulations? The answer can be given only by a direct comparison with the experiment, but

unfortunately an experiment with an outcome describing the structure and dynamics of water at the metal-solution interface is not available yet. Nevertheless, it is very encouraging to see that the structural and dynamical properties of water monolayer and water clusters on the surface are in good agreement with the models proposed by the experimentalists.²⁰

From our simulation and the other simulations we observe that the structure of the water layer adjacent to the surface is very sensitive to the nature of the surface and even its geometry. But we also observe that a common feature exists in all the simulations of water at the interfaces. As the simulations show, even a very strong perturbation induced by the surface on the adjacent water layer decays over the distance of ~ 1 nm. This is also true in the present simulation, where a quick change in the behavior of water occurs over a distance of only a few angstrom. While water displays solid-like behavior in the adsorbate layer, the water layer next to it already displays liquid-like behavior. And this is indeed remarkable.

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